

Mass spectrometric speciation of mononuclear Re carbonyls in the gas phase

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For the chemical characterization of bohrium carbonyls, $\text{Bh}(\text{CO})_n$, a gas-phase chemical study of rhenium (Re) carbonyls was conducted at RIBF, RIKEN.¹⁾ However, the experiments provided low chemical yields, making it necessary to further study the formation of mononuclear Re carbonyls. In this study, a laser-ablation time-of-flight mass-spectrometer (LA-TOF-MS) was modified to obtain the mass spectra of mononuclear Re carbonyl ions. High-purity CO and He gas mixtures were used to deduce the most stable species. Moreover, the influence of impurities on the formation of the carbonyls was also investigated by adding O_2 and H_2 to the gas mixture, because both were expected to have a significant influence on Re.²⁾

Figure 1 shows the schematic of our LA-TOF-MS setup. Each measurement starts with the pulse valve opening (120 μs), thereby releasing a supersonic gas jet. The gas is directed over the target surface, where an ablation laser (Nd: YAG laser, 532 nm, 10 Hz, 15 mJ/pulse) induces a plasma to generate free metal atoms and ions. Some of the plasma is rapidly cooled by the gas. Then it is transported through a skimmer to a positive electric field, where a short pulsed high voltage is applied (20 μs , 10 Hz, +1400 V). After free drifting, the cations reach a micro-channel plate (MCP) detector and the flight time is measured. An extension pipe (*i.d.* = 4 mm; length = 60 mm) is added downstream of the metal target in to increase the reaction time and strengthen the interaction between Re ions and CO gas. This was done to identify the most stable products formed in the gas phases, which are similar to those of our gas chromatography experiment.^{1,3)}

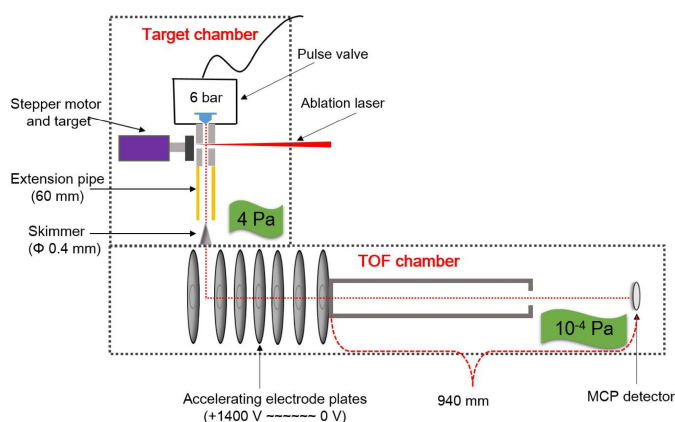


Fig. 1. Schematic of the LA-TOF-MS technique.

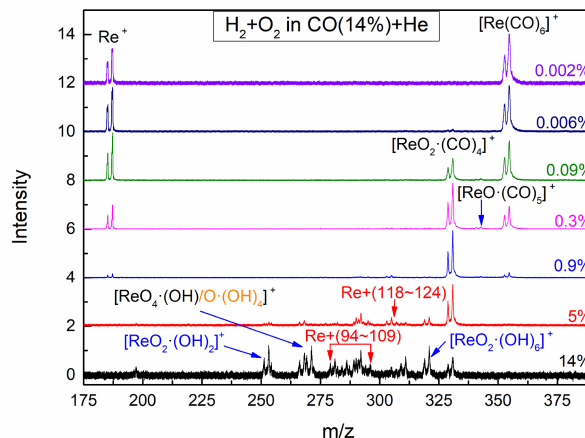


Fig. 2. Mass spectra with a Re target using H_2 and O_2 in CO and He gas mixture (C_{CO} is 14%, while both C_{H_2} and C_{O_2} vary from 14% to 0.002% in the same steps).

Because the ion mass is proportional to the square-root of its flight time, the mass number of each cation can be determined, and then the chemical formula can be deduced. Using He seeded by CO ($C_{\text{CO}} = 14\%$) as the carrier gas, Re^+ and $[\text{Re}(\text{CO})_6]^+$ ions can be clearly identified in the mass spectrum. No intermediates or other products can be observed owing to the added extension pipe. Then, H_2 , O_2 , and H_2/O_2 gas mixtures are added to the carrier gas as impurities. Only few $[\text{Re}(\text{CO})_5 \cdot (\text{H}_2)]^+$ can be observed when 14% of H_2 is added to the carrier gas. No other Re carbonyl hydrides appear when C_{H_2} is lower than 5%, while large amount of $[\text{ReO}_2 \cdot (\text{CO})_4]^+$ can be observed when O_2 is added to the carrier gas. Therefore, H_2 does not have a significant influence on the formation of $[\text{Re}(\text{CO})_n]^+$. The mass spectra of O_2 gas mixtures are very similar to Fig. 2. Figure 2 shows the mass spectra of adding H_2 and O_2 to the CO and He carrier gas (C_{CO} was fixed at 14%; C_{H_2} and C_{O_2} varied from 14% to 0.002% in the same steps). Despite the small quantities of hydroxides visible in both figures, the only significant reaction products are $[\text{ReO}_2 \cdot (\text{CO})_4]^+$ and $[\text{Re}(\text{CO})_6]^+$. $[\text{ReO}_2 \cdot (\text{CO})_4]^+$ disappears completely when C_{O_2} is 0.002%. Therefore, we conclude that the formation of Re carbonyl ions is not sensitive to trace amounts of H_2 , while even 0.09% of O_2 will significantly increase the product yield of Re carbonyl oxide ions and decrease the product yield of Re carbonyl ions.

References

- 1) Y. Wang *et al.*, RIKEN Accel. Prog. Rep. **50**, 25 (2017).
- 2) Y. Wang *et al.*, Phys. Chem. Chem. Phys. **17**, 13228 (2015).
- 3) Y. Wang *et al.*, Phys. Chem. Chem. Phys. **21**, 7147 (2019).

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